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| 14. ABSTRACT Research supported by this grant entitled "Passive Sensor Materials Based on Liquid Crystals" revolved around an investigation of liquid crystalline materials for use in passive sensors for chemical agents, including sulfur and phosphorus-containing compounds. The research was founded on the discovery in the Abbott research group at University of Wisconsin that competitive molecular interactions between metal ion receptors, liquid crystals and targeted analytes can lead to easily visualized and quantified changes in the orientations of films of liquid crystals. | | | | | |
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Report Title

Passive Sensor Materials based on Liquid Crystals

ABSTRACT

Research supported by this grant entitled “Passive Sensor Materials Based on Liquid Crystals” revolved around an investigation of liquid crystalline materials for use in passive sensors for chemical agents, including sulfur and phosphorus-containing compounds. The research was founded on the discovery in the Abbott research group at University of Wisconsin that competitive molecular interactions between metal ion receptors, liquid crystals and targeted analytes can lead to easily visualized and quantified changes in the orientations of films of liquid crystals. These changes in optical appearance of the liquid crystal offer the basis of a new approach for measurement and monitoring of exposure to specific and non-specific chemical environments. Selective detection of simulants of G agents and mustard gas in the part-per-billion concentration (in vapor) on time scales of tens of seconds was demonstrated. Tolerance to potentially interfering compounds (e.g., water) at concentrations 100,000 times higher than the targeted simulants was also shown. Research described in this report focused on the translation of these past findings into the design of nanostructured liquid crystalline materials that exhibited the sensitivity and specificity demonstrated in past studies with the added benefits of (i) mechanical robustness and (ii) processability such that a range of potential DoD applications are enabled.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Katie D. Cadwell, Nathan A. Lockwood, Barbara A. Nellis, Mahriah E. Alf, Colin Willis, and Nicholas L. Abbott, “ Detection of organophosphorous nerve agents using liquid crystals supported on chemically functionalized surfaces”. *Sensors and Actuators B, Chemical*, 128, 91-98, 2007

Koenig, G. M., Jr.; Gettelfinger, B. T.; de Pablo, J. J.; Abbott, N. L. Using Localized Surface Plasmon Resonances to Probe the Nanoscopic Origins of Adsorbate-Driven Ordering Transitions of Liquid Crystals in Contact with Chemically Functionalized Gold Nanodots *Nano Lett.* 8(8); 2362-2368, 2008.

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Gettelfinger, BT; Moreno-Razo, JA; Koenig,; Hernandez-Ortiz, JP; Abbott, NL; de Pablo, JJ "Flow induced deformation of defects around nanoparticles and nanodroplets suspended in liquid crystals" *Soft Matter*, 6 (5): 896-901 2010.

Koenig, GM; Lin, IH; Abbott, NL "Chemoresponsive Assemblies of Microparticles at Liquid Crystalline Interfaces", *Proceedings of the National Academy of Sciences*, 107 (9), 3998-4003, 2010.

Kinsinger MI, Buck ME, Meli MV, Abbott, NL, Lynn DM, "Langmuir Films of Flexible Polymers Transferred to Aqueous/Liquid Crystal Interfaces Induce Uniform Azimuthal Alignment of the Liquid Crystal", *Journal of Colloid and Interface Science*, 341 (1) 124-135, 2010

Number of Papers published in peer-reviewed journals: 24.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

None

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

ACS Colloids Symposium, NCSU, June 2008

MRS meeting in San Francisco, March, 2008

GRC on Chemistry at Interfaces, Waterville Valley, July, 2008

AIChE meeting in Salt Lake City, November, 2007.

Abbott, N.L. "Amplification of Biomolecular Interactions using Liquid Crystals", Keynote Lecture at Soft Matter Symposium, ACS Colloid and Surface Science Meeting, North Carolina State University, June 2008.

Abbott, N.L. "Nanostructure of Complexes of DNA and Redox-Active Surfactants for Spatial and Temporal Control of Transfection", International Conference on Bionanotechnology, Dublin, Ireland, July, 2008.

Abbott, N.L., "Colloidal Interactions in Liquid Crystals", Departmental Seminar, Chemical Engineering, Virginia Tech, October, 2008.

Abbott, N.L. "Biomolecular Analysis based on Liquid Crystals", Innovative Molecular Analysis Program, National Cancer Institute, Cambridge, MA, October, 2008.

Abbott, N.L., "Amplification of Biomolecular Interactions Based on Liquid Crystals", Departmental Seminar, Chemical Engineering, Northwestern University, November, 2008.

Abbott, N.L. "Optical Sensors for Biomolecules" Materials Research Society Meeting, December, 2008

Abbott, N.L. "Colloids Interactions in LC Systems", ARO Workshop, Napa, CA, March, 2009.

Abbott, N.L., "Amplification of Molecular Interactions using Liquid Crystals", University of Pittsburgh, PA, April 2009.

5th US-Sino Conference on Chemical Engineering, October 2009, Beijing "Colloidal and Interfacial Phenomena involving Liquid Crystals"

ACS Meeting, DC, August 2009 "Directed Assembly of Colloids at Interfaces of Liquid Crystals"

Columbia University, February, 2010, "Novel Colloidal and Interfacial Phenomena in Liquid Crystalline Systems"

CBD Conference, November 2009, "Novel Materials based on Liquid Crystals that Respond to Targeted Chemical and Biological Environments"

MIT, November 2009 "Novel Colloidal and Interfacial Phenomena in Liquid Crystalline Systems"

ACS Meeting, San Francisco, March 2010 "Ordering Transitions at Aqueous-Liquid Crystal Interfaces Decorated with Functional Amphiphilic Polymers"

ACS Meeting, San Francisco, March 2010 "Optically Responsive and Mechanically Tunable Colloid-in-Liquid Crystal Gels that Support Growth of Fibroblasts"

Brandeis University, February 2010, "Novel Colloidal and Interfacial Phenomena in Liquid Crystalline Systems"

Number of Presentations: 22.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Optically Responsive and Mechanically Tunable Colloid-in-Liquid Crystal Gels, filed with USPTO, 2008.

Monodisperse Emulsions through Templating Polyelectrolyte Multilayer Capsules, filed with USPTO, 2008.

Immobilization of Droplets of Liquid Crystals on Surfaces, filed with USPTO, 2009.

Patents Awarded

Awards

2011, Plenary Lecture, 11th European Conference on Liquid Crystals (Slovenia)

2011, Vilas Associate, University of Wisconsin-Madison

2011, AAAS Fellow

2010, Charles M.A. Stine Award of AIChE for Materials Research

2010, Technology Achievement Award, MIT Club of Wisconsin for Platypus Technologies LLC

Graduate Students

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| Jacob Hunter | 0.50 |
| Katie Cadwell | 0.25 |
| Gary Koenig | 0.25 |
| FTE Equivalent: | 1.00 |
| Total Number: | 3 |

Names of Post Doctorates

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| Santanu Pal | 0.50 |
| Yang, Zhongqiang | 0.25 |
| FTE Equivalent: | 0.75 |
| Total Number: | 2 |

Names of Faculty Supported

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> | National Academy Member |
|------------------------|--------------------------|-------------------------|
| Nicholas L. Abbott | 0.05 | No |
| FTE Equivalent: | 0.05 | |
| Total Number: | 1 | |

Names of Under Graduate students supported

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

| | |
|--|------|
| The number of undergraduates funded by this agreement who graduated during this period: | 0.00 |
| The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... | 0.00 |
| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... | 0.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: | 0.00 |

Names of Personnel receiving masters degrees

| |
|----------------------|
| <u>NAME</u> |
| Total Number: |

Names of personnel receiving PhDs

| |
|----------------------|
| <u>NAME</u> |
| Katie Cadwell |
| Gary Koenig |
| Total Number: |

Names of other research staff

| | |
|------------------------|--------------------------|
| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
| FTE Equivalent: | |
| Total Number: | |

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Research supported by 50494-CH, “Passive Sensor Materials Based on Liquid Crystals”, revolved around investigation of liquid crystalline materials for use in passive sensors for chemical agents, including sulfur and phosphorus-containing compounds. The research was founded on the discovery in the Abbott research group at University of Wisconsin that competitive molecular interactions between metal ion receptors, liquid crystals and targeted analytes can lead to easily visualized and quantified changes in the orientations of films of liquid crystals. These changes in optical appearance of the liquid crystal offer the basis of a new approach for measurement and monitoring of exposure to specific and non-specific chemical environments. Selective detection of simulants of G agents and mustard gas in the part-per-billion concentration (in vapor) on time scales of tens of seconds has been demonstrated. Tolerance to potentially interfering compounds (e.g., water) at concentrations 100,000 times higher than the targeted simulants was also shown. Experiments also confirmed selective detection of GA, GB, GD and VX. The goal of the research supported under 50494-CH was to translate these past findings into the design of nanostructured liquid crystalline materials that exhibit the sensitivity and specificity demonstrated in past studies with the added benefits of (i) mechanical robustness and (ii) processability such that a range of potential DoD applications are enabled.

Several broad strategies leading to the design of liquid crystalline materials for sensing were pursued: (i) chemically functionalized solid particles dispersed in liquid crystals, and (ii) liquid crystalline droplets “wrapped” in ultrathin shells of functional polymers. A key element of both approaches was to make use of polyelectrolyte multilayer films that incorporate ligands that bind metal ions and orient liquid crystals. These two classes of nanostructured liquid crystalline materials are easily processed and the high internal surface areas of these materials offer the basis of even higher sensitivities than those reported in the past. The results of this research enable new approaches for optical transduction of ordering transitions in liquid crystals induced by targeted chemical agents. The dynamic optical response of these materials to simulants of warfare agents was studied. Tolerance to potentially interfering compounds was also investigated.

Key advances achieved during this research grant are summarized below.

Part 1. Formation of PEMs that Incorporate Metal Ions

As mentioned above, a key element of approaches that we pursued during the grant period involved the use of polyelectrolyte multilayer films that incorporated metal ions that bind and thereby orient liquid crystals. To this end, we demonstrated that it is possible to prepare polyelectrolyte multilayer films (PEMs) composed of layers of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) (Figure 1) that incorporate metal ions and orient liquid crystals. Initial studies focused on incorporation of Al^{3+} into the PEMs. The formation of the PEMs was confirmed using ellipsometry, as shown in Figure 2. The PEMs were prepared by dipping substrates to be coated in a solution that contained 4mg/ml polyelectrolyte, 0.5M NaCl, 100mM $\text{Al}(\text{ClO}_4)_3$ in deionized water, where the pH was adjusted to 3.5 using HCl, for 4 minutes followed by a two minute rinse in deionized water.

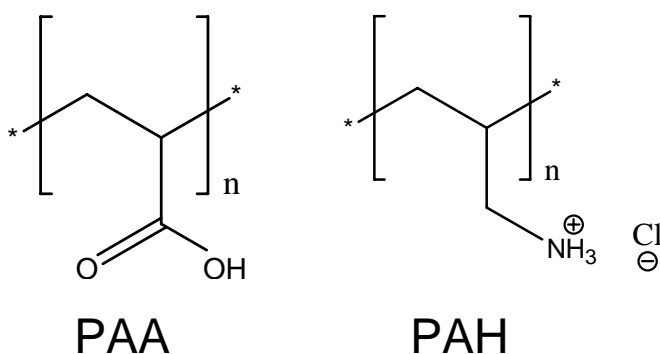


Figure 1. Structure of polyelectrolytes: poly(acrylic acid), PAA, and poly(allylamine hydrochloride), PAH.

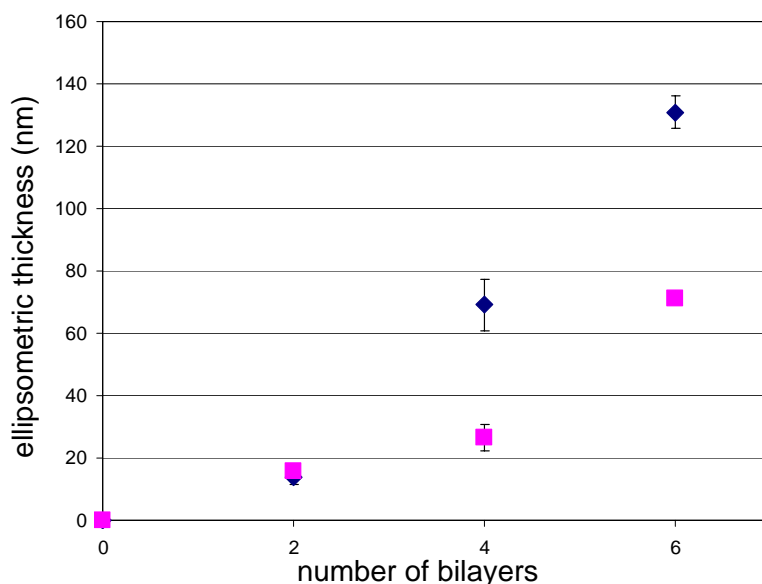


Figure 2. Ellipsometry measurements of PEMs formed on gold coated silicon wafers with an Al^{3+} salt (pink square) and without a metal salt (blue diamond).

We demonstrated that incorporation of a trivalent metal ion into the PEMs allowed the orientation of the liquid crystal (LC) to be controlled through the metal ion-LC coordination interactions. These experiments were performed by depositing a PEM onto a gold film, and hosting liquid crystal within a gold specimen grid placed onto the PEM. As shown in Figure 3, the PEM that incorporated the Al^{3+} salt caused a perpendicular orientation of the nematic liquid crystal with nitrile groups (5CB) whereas the PEM without Al^{3+} salts led to an orientation of the LC that was parallel to the surface.

We also verified that exposure of the nematic 5CB supported on the Al^{3+} salts led to an orientational transition. In these experiments, we fabricated microwells to host the liquid crystals. Polyurethane (PU) microwells with a width of $500\mu\text{m}$ and a depth of

2.8 μ m were coated in gold and soaked in a 2mM solution of 11-mercaptoundecanoic acid in ethanol for 1 hr. Following functionalization of the PU microwells, PEMs containing aluminum salts were deposited onto the surface following the procedure described above. The PU microwells were then filled with liquid crystal which resulted in homeotropic anchoring, as shown in Figure 4A. Treatment of the PU microwells with 10ppb DMMP led to a change in the liquid crystal orientation within approximately tens of seconds, as shown in Figure 4B. This change in ordering was caused by the coordination of the metal ion with the DMMP which disrupts the metal ion-nitrile (5CB) interaction. When the system was purged with air the 5CB returned to the homeotropic anchoring, as shown in Figure 4C. This cycle was repeated, as is shown in Figure 4.

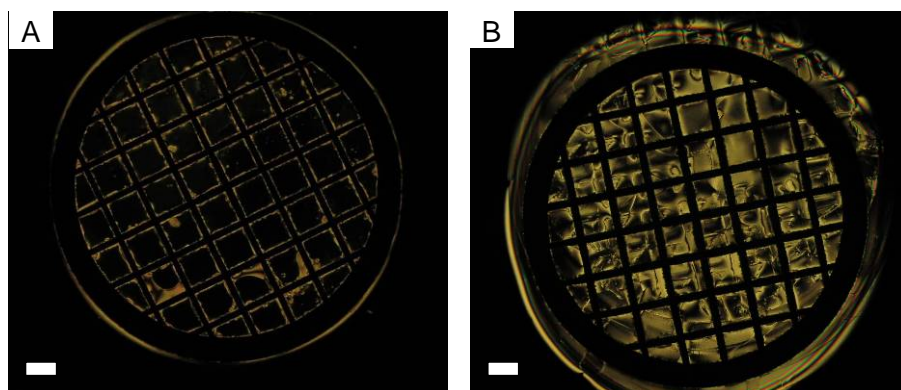


Figure 3. Optical image of liquid crystals, 5CB, in contact with a gold substrate that was coated with 5 bilayers of PAH/PAA A) with 100mM $\text{Al}(\text{ClO}_4)_3$ and B) without Al salt. The liquid crystals were hosted in a TEM grid. Scale bar 250 μ m

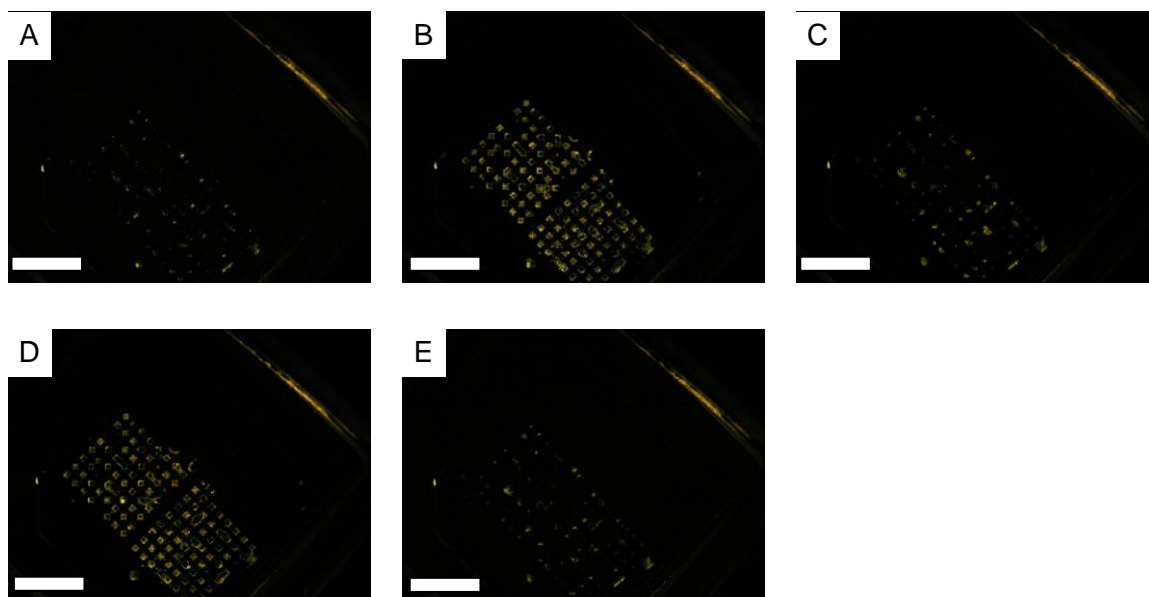


Figure 4. Optical response of 5CB. A) Initial orientation B) after 30seconds of exposure to 10ppb DMMP C) after purging the system with air for 10 minutes D) after 30seconds

of exposure to 10ppb DMMP E) after purging the system with air for 10 minutes. Scale bar 0.5cm.

The results above provided an exciting demonstration that PEMs can be used to host metal ions on surfaces such that the metal ions orient liquid crystal through coordination interactions. When an analyte is present that competes with the nitrile group for coordination with the metal ion, an orientational transition is observed in the liquid crystal. Additional experiments performed during the course of the grant demonstrated that other metal ions can be incorporated into the PEMs to manipulate the selectivity of the response of the liquid crystal. As described below, an important objective of our research was to integrate PEMs into LC composite materials to create chemically-responsive composite materials that are easily processed.

Part 2. Formation of Colloidal Crystals and Infiltration with Liquid Crystals.

We performed a series of investigations that investigated the design of LC-based composite materials that involved dispersions of colloidal particles in liquid crystals. These designs included periodic organizations of colloidal particles (i.e., colloidal crystals) as well as random networks of colloidal particles, that led to demonstrations of LC gels (see below). Here we describe the studies involving colloidal crystals.

Several different techniques were investigated to make colloidal crystals using polystyrene (PS) spheres (monodisperse microspheres with a diameter of 269nm purchased from Duke Scientific). The first approach involved the use of a microfluidic cell into which a suspension of microspheres was pumped: the outlet of the microfluidic cell was designed such that liquid could exit but not spheres (see Xia, *Langmuir*, 2001, **17**, 6344). This technique had several drawbacks. First, the particles often leaked out of the system and, second, the thickness of the crystal did not appear to be uniform. A second approach involved use of a Teflon ring with an inner diameter of 1cm that was clamped between two metal plates to form a deposition chamber. The aqueous suspension of particles was placed into the deposition chamber and then spread on a glass quartz slide that had been cleaned following the RCA protocol. (*Advanced Materials*, **14**, 1160) While this technique did not suffer the leakage problems that occurred using the first technique, it also resulted in the formation of non-uniform particle arrays. The third technique that was investigated was a so-called vertical deposition method (*Chem. Mater.*, 1999, **11**, 2132). With this technique, a glass slide cleaned following the RCA protocol was suspended in an aqueous suspension of particles. The sample was incubated in the presence of saturated LiCl_2 to control the rate of solvent evaporation, thus resulting in the formation of a crystal array (Figure 5).

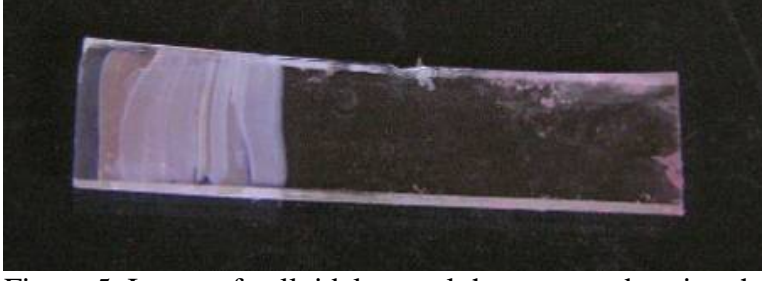


Figure 5. Image of colloidal crystal that was made using the vertical deposition method.

Colloidal crystals of the type shown in Figure 5 exhibited optical stop bands at $\sim 630\text{nm}$, as shown in Figure 6. The peak wavelength of the optical stop band can be calculated approximately assuming the Bragg diffraction under normal incidence as

$$\lambda = 2\sqrt{2/3}d(n_{\text{eff},\text{matrix}}^2 f + n_{\text{particle}}^2 (1-f))^{1/2}$$

where λ is the peak position of the optical stop band, d is the diameter of the spheres, f is the void fraction within the colloidal crystals, and $n_{\text{eff},\text{matrix}}$ and n_{particle} are the effective refractive indices of the interstitial space and particles. For the system we investigated, $d = 269\text{nm}$, $n_{\text{eff},\text{air}} = 1$, $n_{\text{PS}} = 1.59$, and $\lambda \sim 630\text{nm}$. The Bragg diffraction equation was used to calculate the void fraction, f , of the particle array as $f = 0.31$, which is indicative of a face centered cubic crystal. The colloidal crystals were found to be mechanically robust and thermal annealing of the crystals resulted in a slight change in the peak absorbance, but no significant change in peak position, as shown in Figure 7.

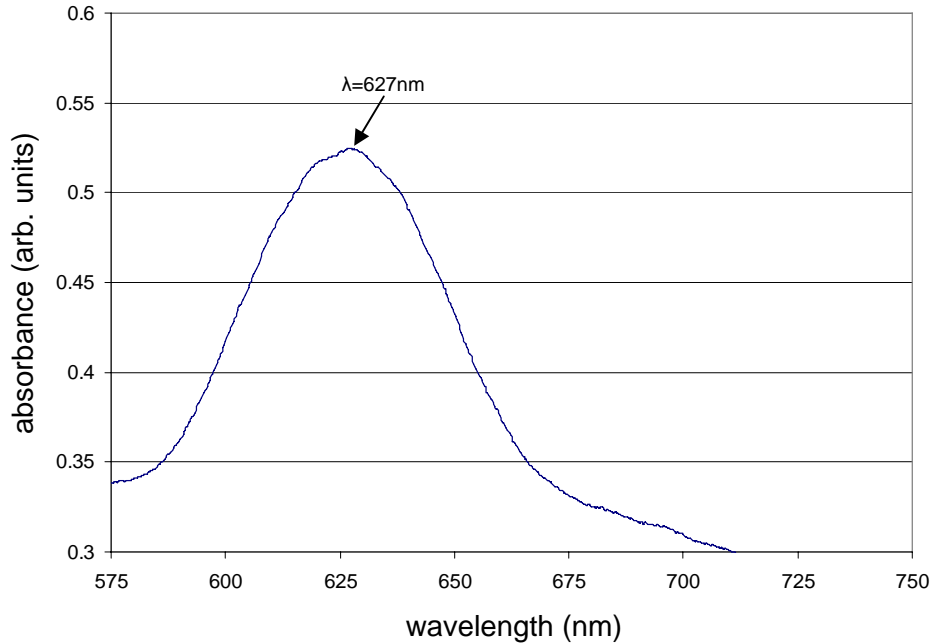


Figure 6. Absorbance spectra of colloidal crystal in air.

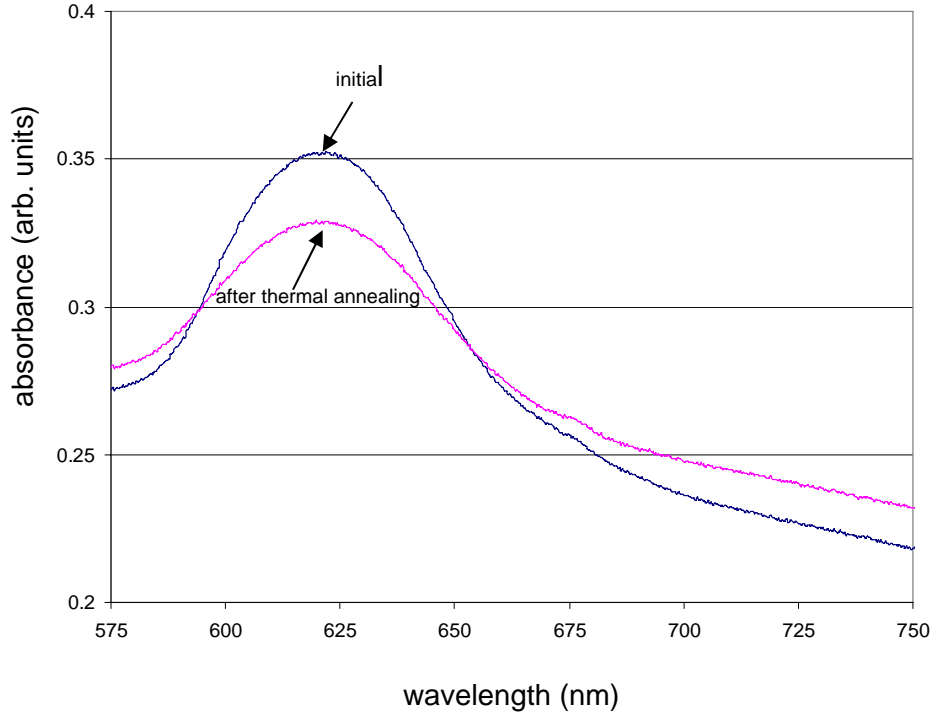


Figure 7. Absorbance spectra of colloidal crystal in air, before and after thermal annealing at 85°C for 30minutes.

Infiltration of the colloidal arrays with a solvent (e.g. water) was observed to lead to changes in the position of the optical stop bands due to the change in the refractive index of the medium in the interstitial space. Figure 8 shows the change that occurred upon introduction of water. The peak corresponding to the optical stop band was measured at $\lambda \sim 625\text{nm}$, and using the Bragg equation, the void fraction was calculated to be $f = 0.33$. Using the value of $f = 0.33$ and $n_{\text{water}} = 1.33$, the position of the peak was calculated to be $\lambda = 663\text{nm}$. We measured the peak to occur at $\lambda = 652\text{nm}$. The difference between measured and calculated values may be the result of the incomplete infiltration of the water into the voids.

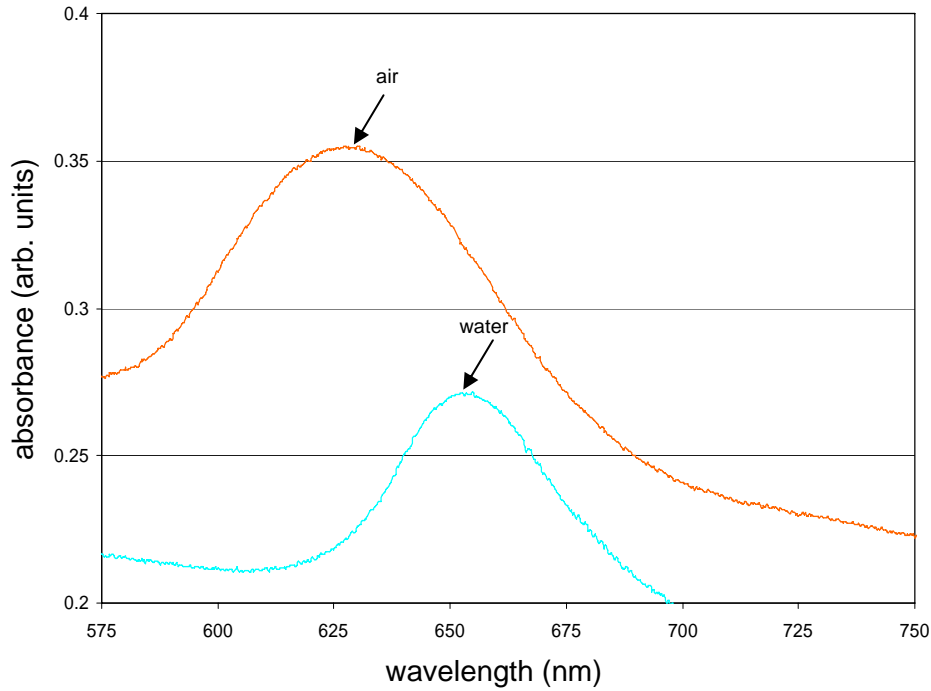


Figure 8. Absorbance spectra of colloidal crystal in air and after infiltration with water.

We subsequently established several different techniques to infiltrate the colloidal crystals with liquid crystal. The preferred procedure emerging from our efforts involved the placement of a drop of liquid crystal mixed with ethanol (1:1 volume mixture) onto the edge of the colloidal crystal. The sample was then left in air overnight, to allow for evaporation of the ethanol. UV absorbance measurements are shown in Figure 9. The absorbance peak corresponding to the stop band in air was at $\lambda \sim 618\text{nm}$, refer to figure 9, corresponding to a void fraction $f=0.36$. Using a value of $f = 0.36$ and $n_{E7} = 1.61$, the position of the peak was calculated to shift to $\lambda = 702\text{nm}$. Figure 9 reveals very close agreement between calculation and experiment.

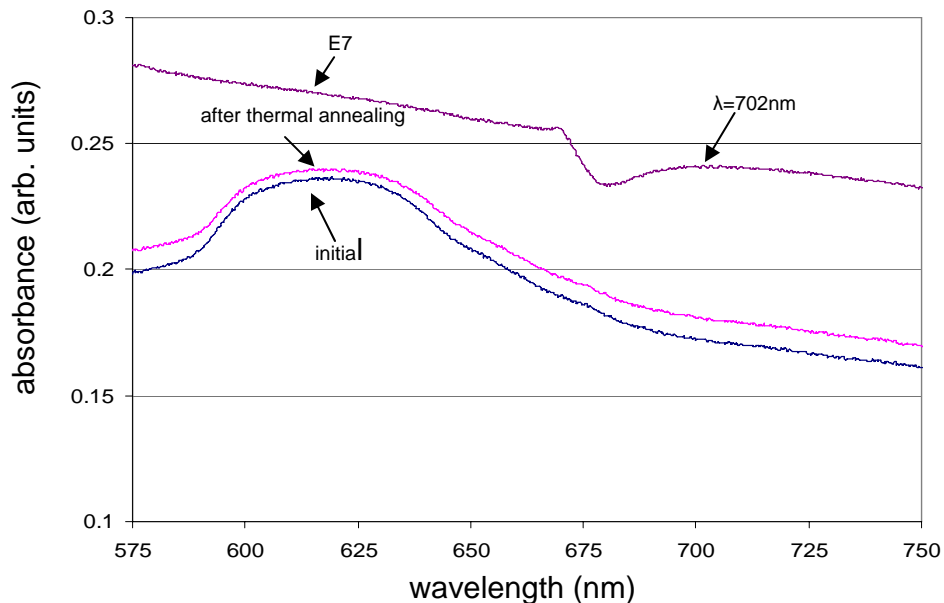


Figure 9: Absorbance spectra of colloidal crystal before and after thermal annealing (85°C for 30minutes) and after infiltration with liquid crystal (E7).

The results above demonstrate the preparation of colloidal crystals infiltrated with liquid crystals. Building on this accomplishment, we investigate the deposition of PEMs onto the colloids (as described above), so as to create chemically-responsive photonic materials. The samples that had been thermally annealed were coated with PEMs following the procedure described above. Deposition of the PEM onto the particle arrays led to an increase in the sample absorbance, as shown in Figure 10. When the coated PEMs were infiltrated with liquid crystal, E7, the absorbance peak corresponding to the optical band gap was observed at $\lambda \sim 715\text{nm}$ (Figure 11). Subsequent exposure of these materials to DMMP led to demonstrations of changes in the optical band gaps of these materials. This result demonstrated the feasibility of making chemically responsive, photonic materials using surface-functionalized particles dispersed in liquid crystals.

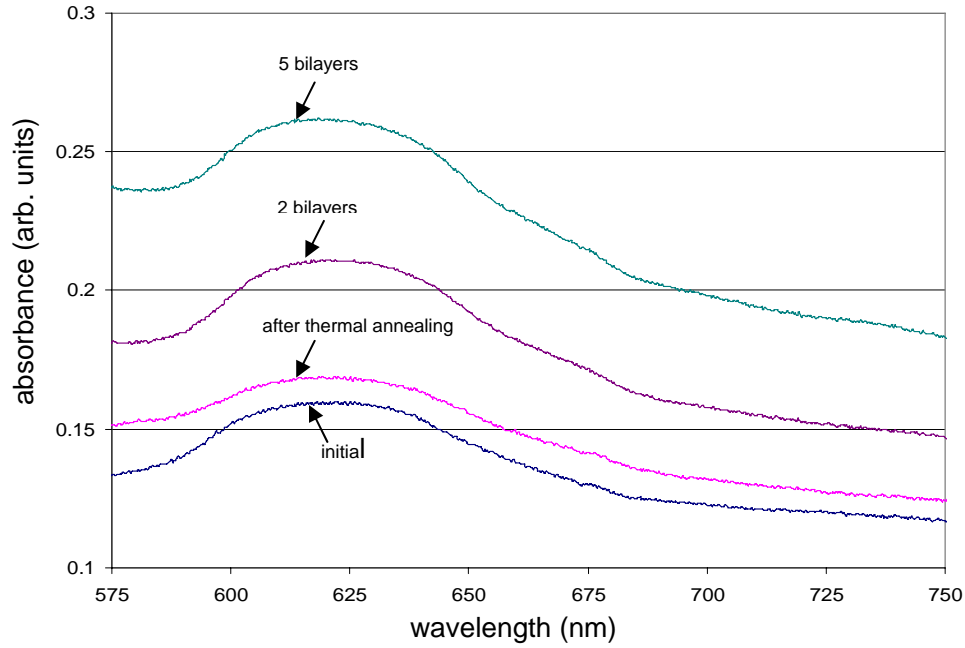


Figure 10: Absorbance spectra of colloidal crystal before and after thermal annealing (85°C for 30minutes). After deposition of PEM, 2 and 5 bilayers, respectively.

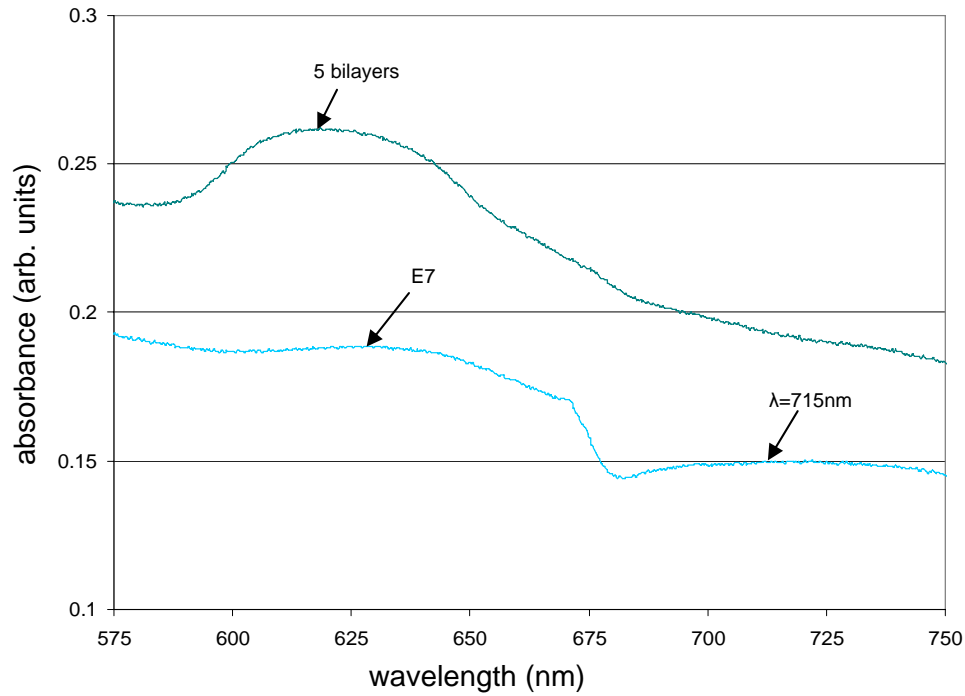


Figure 11: Absorbance spectra of colloidal crystal that had been coated with 5 bilayers of PEs both before and after its infiltration with liquid crystal (E7).

Part 3. Chemically Responsive Liquid Crystalline Gels Prepared from Colloidal Dispersions in LCs.

Whereas the results described above, involved the using of periodic arrays of colloidal particles dispersed in LCs, during the course of the grant period, we also investigated the formation of chemically responsive LC gels formed from random dispersions of colloidal particles. This exciting advance has led to self-supporting and mechanically robust colloid-in-LC (CLC) gels that can be molded, easily handled and processed yet retain their responsiveness to chemical species. These gels were prepared by dispersing polystyrene colloidal particles (PS, 1 μm in diameter) into low molecular weight liquid crystals (5CB, E7). A mixture comprising particles and mesogens (10% PS in E7) in the isotropic state was allowed to cool at a fixed rate (0.5 $^{\circ}\text{C}/\text{min}$), which resulted a mechanically stable network of colloids (Figure 12A), that led to the formation of gels, possessing micrometer sized dynamic liquid crystal domains that are separated by colloids (Figure 12B).

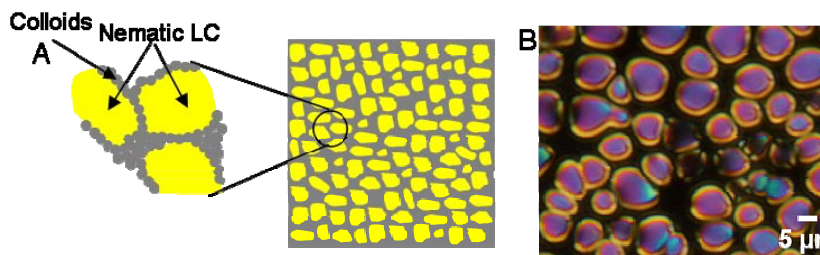


Figure 12. (A) Schematic showing the formation of a CLC gel. (B) A μm -thin film of CLC gel displaying micrometer sized ($\sim 10 \mu\text{m}$ diam) domains of dynamic liquid crystals that are separated by colloids.

We formed the CLC thin film on a metal ion functionalized surfaces and demonstrated that it is possible to trigger orientational transitions within the CLC gel. To make a thin film, we confined the CLC between two chemically functionalized (here, CuCl_2O_8) gold coated glass slides with spacers of desired thickness (2 μm). The average film thickness of the CLC sample was determined to be $\sim 1 \mu\text{m}$. A large number of domains appeared dark under crossed polars (Figure 13, 0s), indicating LC domains were homeotropically aligned in the LC-rich domain. The nitrile groups of E7 weakly bind with surface-immobilized Cu^{2+} ions and thus dictate the homeotropic anchoring of LC. When we exposed these functionalized CLC film to vapors of DMMP (ppm concentration), a CWA simulant, the high affinity of DMMP for Cu^{2+} , leads to displacements of LC from their metal ion complex and an easily visualized change of LC domain from dark to bright (Figure 13, 80s). These results demonstrate the basis of a class of responsive LC materials that would be easily processes and mechanically robust.

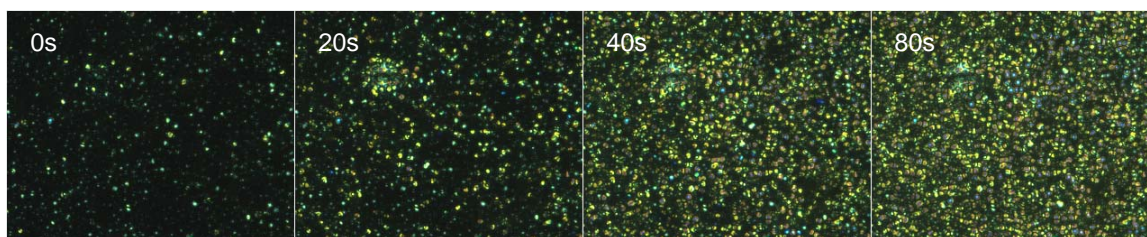


Figure 13. Adsorbate-induced transition in the anchoring of LC molecules in a 1 μm thin film of CLC gel hosted on Cu^{2+} functionalized gold-coated glass slides. CLC thin film exposed to DMMP showing transitions of LC from dark (0s) to bright planar orientation (80s).

Part 4. Fabrication of Polymer Capsules Filled with Liquid Crystals.

As described above, a key accomplishment of our research during the period of this grant was the demonstration that polyelectrolyte multilayers (PEMS) impregnated with metal ions can be used to orient LCs, and to create LC composite materials that respond to organophosphonate compounds. We subsequently built on this result to develop methods based on PEMS that yield monodisperse LC droplets wrapped in a shell of polyelectrolytes. These “wrapped” LC droplets offer the basis of a broadly robust and processable class of responsive LC-based materials. They are ideally suitable for preparation of colloidal crystalline arrays that would change their optical properties (e.g., photonic band gaps) upon exposure to targeted chemical species (see above). The methodology is based on templating PEM capsules formed by the layer-by-layer (LbL) adsorption of polyelectrolytes on sacrificial particles, to produce a range of emulsions of a predetermined size (Figure 14). The silica particles ($5 \pm 0.5 \mu\text{m}$) were first amine-functionalized by grafting 3-aminopropyltriethoxysilane (APTS) to the particle surface. The APTS-functionalized silica particles were next coated with PEMs, and the coated particles were exposed to hydrofluoric acid (HF) to etch the silica core, resulting in the formation of hollow PEM capsules.

We investigated two types of polyelectrolyte capsules: electrostatically coupled poly(sodium-4-styrenesulfonate) (PSS) and poly (allylamine hydrochloride) (PAH); and hydrogen-bonded poly(methacrylic acid) (PMA) and poly(vinylpyrrolidone) (PVPON). These PEMs have been well-studied and were chosen because the PSS/PAH capsules are highly stable under different conditions, whereas the PMA/PVPON capsules can be readily disassembled due to weakening of the hydrogen bonding between the layers by changing the pH. After etching of the silica cores with HF, the capsules were washed five times with water and twice with ethanol, 5CB was infiltrated through the semipermeable walls of the PEM capsules, and excess 5CB was removed from outside of the PEM capsules by contacting the capsules with water. This procedure resulted in formation of monodisperse PEM-coated LC droplets (denoted as $5\text{CB}-(\text{PSS}/\text{PAH})_4$ or $5\text{CB}-(\text{PMA}/\text{PVPON})_4$). Naked LC emulsion droplets were prepared by disassembling the PMA/PVPON layers upon exposure to pH 7.5

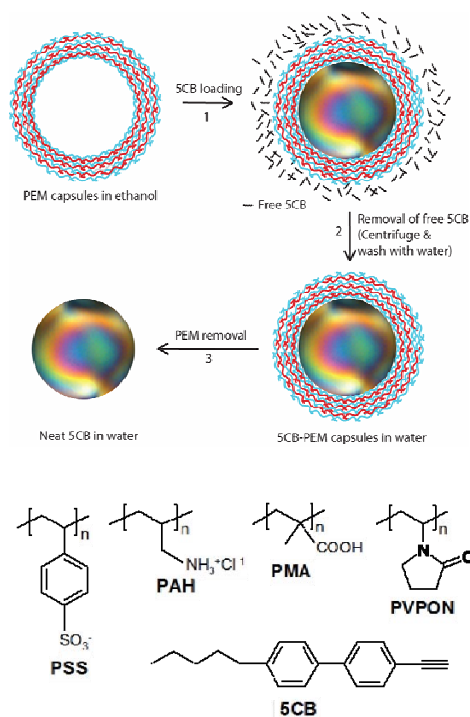


Figure 14. Schematic representation of the procedure used to prepare monodisperse emulsion droplets. Loading of 5CB into the PEM capsules (step 1); removal of 5CB from outside of the capsules (step 2); disassembly of the PEM capsules to produce naked 5CB emulsion droplets (step 3). The inset within the sketch of the capsules is a polarized light micrograph of a 5CB droplet.

solutions. The above-described technique was also extended to other oils (silicone oil and paraffin oil droplets) and the size of capsule templates was also varied (0.7 to 10 μm , Figure 15) to produce monodisperse emulsions of various sizes. This method was found to be robust and can be potentially applied to routinely produce large quantities of naked monodispersed oil droplets ranging from nanometers to micrometers, or oil-droplets functionalized with a variety of PEM coatings that can be tailored for specific applications.

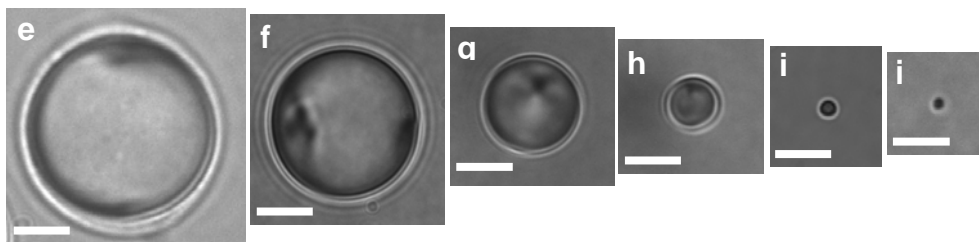


Figure 15: Bright-field micrographs of polymer-encapsulated 5CB droplets obtained using silica templates having diameters of $10 \pm 0.22 \mu\text{m}$, $8 \pm 0.20 \mu\text{m}$, $5 \pm 0.19 \mu\text{m}$, $3 \pm 0.18 \mu\text{m}$, $1 \pm 0.04 \mu\text{m}$ or $0.7 \pm 0.08 \mu\text{m}$, respectively. The scale bars in all images correspond to 3 μm .

Part 5. Fabrication of Chemically Responsive LC Gels using Hydrogen-Bonded Gelators.

In addition to the gels described above, which are based on colloidal networks, we investigated liquid crystalline physical gels, a new class of dynamically functional materials consisting of liquid crystals and fibrous aggregates of molecules called “gelators”. They are obtained by the self-assembly of fibrous solid networks of gelators in liquid crystals. They become soft solids by gelation, keeping their stimuli-responsive properties. These LC physical gels are normally formed by thermal processes, in which two independent transitions, the sol-gel transition of a gelator and the isotropic-anisotropic transition of a liquid crystal (Figure 16), are observed. We synthesized two different types of gelators, first one, a simple amino acid derivative, N-Lauroyl-L-alanine (I) (Scheme 1) and the 2nd one is based on L-Lysine, N-Lauroyl-N-stearylaminocarbonyl-L-lysine (II) (Scheme 2).

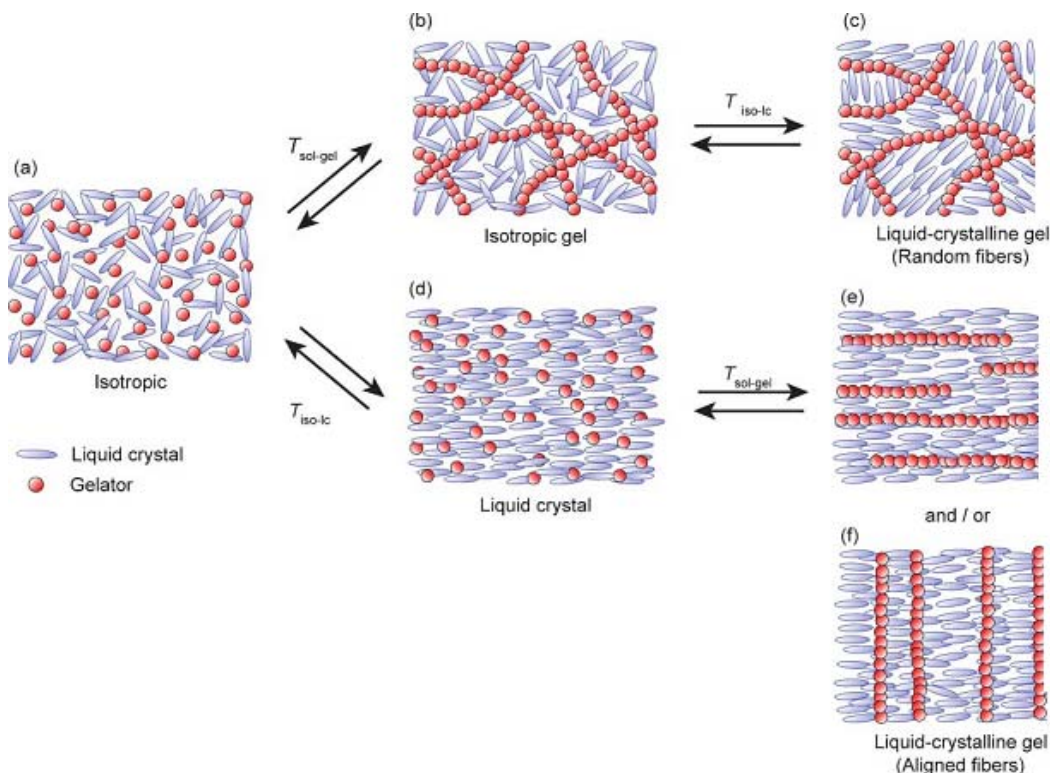
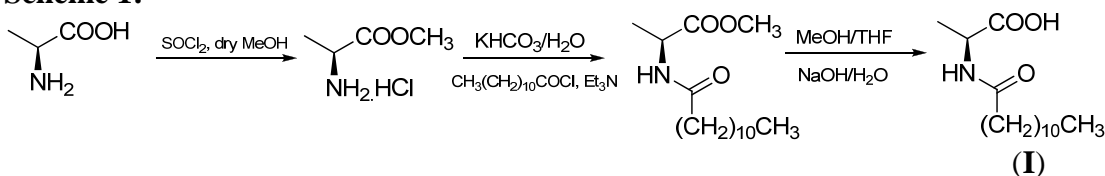
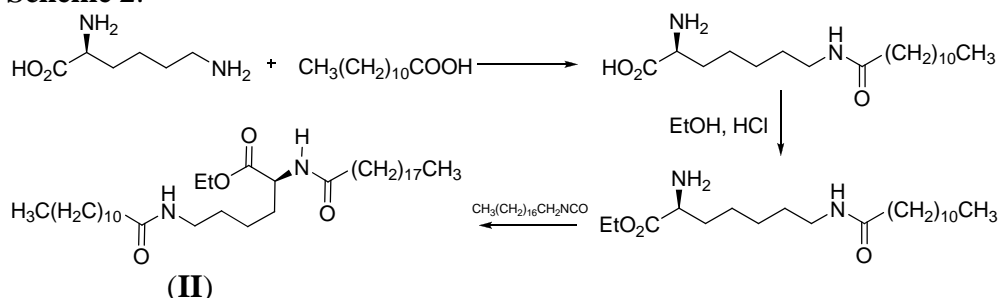
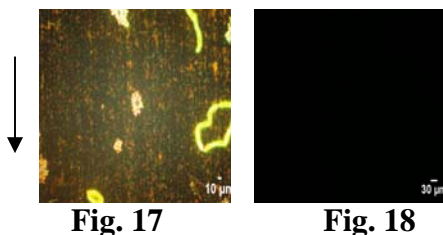


Figure 16. Schematic illustration of two types of thermoreversible structural changes of LC physical gels: $T_{\text{sol-gel}} > T_{\text{iso-lc}}$ ((a)-(b)-(c)); $T_{\text{iso-lc}} > T_{\text{sol-gel}}$ ((a)-(d)-(e,f)).

Scheme 1:**Scheme 2:**

Gelators **I** and **II** were both found to form gels with low molecular weight liquid crystals such as 5CB, E7, 5PCH through non covalent interactions such as hydrogen bonding, π - π interactions. In particular, the gel formed by mixing 0.25 mol% **I** in 5PCH [4-(trans-4-pentylcyclohexyl)-benzonitrile] was found to have a higher isotropic-to-nematic transition temperature as compared to the sol-gel transition temperature. In this case, aligned fibers are formed by the templating effects of orientated liquid crystals on rubbed polyimide-coated glass substrates as shown in Figure 17 (arrow indicates direction of rubbing). To determine if the interfacial conditions can dictate the ordering of liquid crystals in the LC gel, we confined the LC gel between two chemically functionalized (Cu^{2+}) gold coated glass slides as described before. It appears dark under crossed polar as shown in Fig. 18. This result demonstrates that these physical gels formed using low molecular weight gelators offer the basis of materials for chemical sensing through adsorbate-induced transitions.



Figures 17 and 18. Optical micrographs of nematic liquid crystalline gels, aligned on chemically functionalized surfaces. See text for details.

In subsequent studies, we investigated the influence of interfacial adsorbates on the ordering of the hydrogen-bonded gels. In previous studies, the exposure of 5CB to surfactants such as sodium dodecyl sulfate (SDS, anionic) has been shown to cause a rapid ordering transition from a planar to homeotropic orientation of 5CB. We conducted a series of experiments with surfactants using LC gel/aqueous interfaces (0.5 wt% gel in E7) to examine if an ordering transition propagate across the LC gel film. We used a homemade polydimethylsiloxane (PDMS) flow chamber for two reasons: (i) to permit rapid and controlled changes in optical changes and (ii) to facilitate repeated exchange of water and SDS. As seen from Figure 19, in presence of 0.5 mM SDS, an ordering transition was observed that led to planar to a hemotropic orientation of the LC gel. Plots of the average gray scale intensity of LC gel as a function of time illustrate that the ordering transition between planar in presence of water and hometropic in presence of a surfactant are reversible (for several cycles) and these transitions occur in time scales that are on the order of seconds. This result demonstrates that hydrogen-bonded LC gels can undergo surface-induced ordering transitions (first demonstration), and thus that they offer the basis of a new class of responsive LC composite materials.

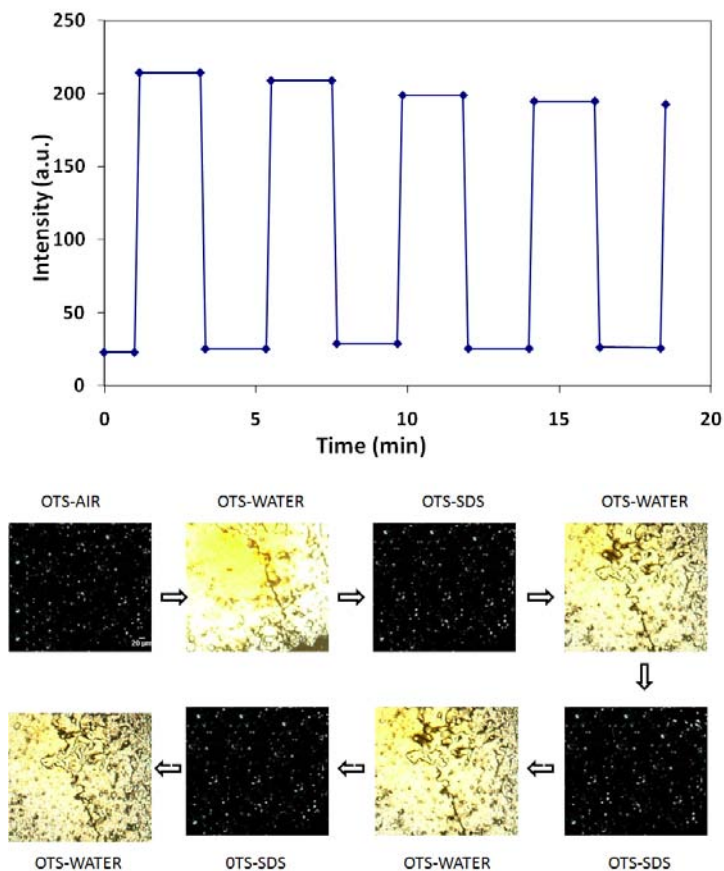


Figure 19. (A) Optical textures (crossed polars) formed by a thin film of gel (0.5 wt% LYS-18 in E7) supported on OTS and subsequently exposed to water and SDS. The concentration of SDS used in the experiment was 0.5 mM (B) Reversibility of optical brightness of the same thin film supported on OTS-coated glass slides that was treated with water and exposed to 0.5 mM SDS.

Part 6. Adsorbate-Induced Ordering Transitions of Nematic Liquid Crystals on Surfaces Decorated with Aluminum Perchlorate Salts

The final thrust of our research performed under support of this grant was focused on providing insight into interfacial physicochemical phenomena underlying adsorbate-induced ordering transitions in nitrile-containing liquid crystals (LCs) supported on surfaces coated with metal perchlorate salts. When the mass density of $\text{Al}(\text{ClO}_4)_3$ deposited onto a surface was low ($0.39 \pm 0.03 \text{ ng/mm}^2$), we measured $20\text{-}\mu\text{m}$ -thick films of nematic 4-cyano-4'-*n*-pentyl-biphenyl (5CB) to initially exhibit perpendicular (homeotropic) ordering, consistent with the influence of coordination interactions between the nitrile groups of 5CB and Al^{3+} ions on the surface on the ordering of the LC. Furthermore, exposure of freshly prepared LC films to vapors of an adsorbate that coordinates strongly to Al^{3+} ions (dimethylmethylphosphonate, DMMP) triggered an ordering transition in the LC films, supporting our conclusion that the initial perpendicular orientation of the LC was induced by nitrile- Al^{3+} coordination interactions. Subsequent equilibration of the LC on the surface (hours), however, resulted in a slow, time-dependent ordering transition in the absence of DMMP that corresponded to the tilting of the LC away from the surface normal. Measurements of the solubility of $\text{Al}(\text{ClO}_4)_3$ in nematic 5CB (saturation value of $1.7 \text{ }\mu\text{mol/ml}$) supported our hypothesis that the slow ordering transition observed in the absence of DMMP was due to the loss of metal ions from the surface into the LC film (dissolution). In contrast, the solubilization capacity of a $20\text{-}\mu\text{m}$ -thick film of 5CB was determined to be insufficient to dissolve $2.14 \pm 0.24 \text{ ng/mm}^2$ of the salt from a surface, and we measured the homeotropic ordering of nematic films of 5CB on these surfaces to persist for days. Equilibration of these samples, however, was accompanied by a loss of response to DMMP (perpendicular orientation of the LC before and after exposure to DMMP). Control experiments performed with a non-coordinating metal perchlorate salt (sodium perchlorate) confirmed our proposition that the loss of response to DMMP was due to formation of an electrical double layer that promoted perpendicular ordering of the LC and thus masked the effects of changes in coordination interactions induced by DMMP on the ordering of the LC (the electric field of the double layer promotes the perpendicular orientation of the 5CB). Finally, by coating surfaces with $\text{Al}(\text{ClO}_4)_3$ at loading that were intermediate to those reported above ($1.13 \pm 0.09 \text{ ng/mm}^2$), we observed (i) perpendicular ordering of the LC in the absence of DMMP, and (ii) reversible ordering transitions induced by DMMP, during storage of samples over 4-5 days. These results, when combined, indicate that the ordering of the LC on the metal salt decorated surfaces is strongly dependent on the loading of metal salt, with key interfacial physicochemical processes being metal ion-nitrile coordination interactions, dissolution of salt into the LC, and formation of electrical double layers. The results of this study provide guidance for the design of LC films that respond to specific chemical analytes and suggest principles for passive chemical sensors.